# <Organic Materials Chemistry> Organic Structural Chemistry

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## Scope of Research

Fundamental studies are being conducted for creation of new functional materials with novel structures and properties. The major subjects are: synthetic and structural studies on novel cyclic π-conjugated systems, particularly the positively charged species stabilized by σ-π interaction; synthesis of new redox-active and supramolecular π-systems; organo-chemical transformation of fullerene $C_{60}$, specifically the synthesis of fullerene dimers and trimers by the use of mechanochemical solid-state reactions; synthesis and reactions of open-cage fullerene derivatives; generation of alkylated $C_{60}$ cation and its application for synthesis of functional materials.

## Research Activities (Year 2002)

### Presentations

Synthesis of New Fullerene Dimers and Open-Cage Fullerenes by Solid-State and Liquid-Phase Reactions of $C_{60}$, Komatsu K, Murata Y, et al., The 201st Meeting of the Electrochemical Society, 16 May, Philadelphia, USA.

The Solvent-Free, Solid-State Reaction of Fullerenes to Give Novel Fullerene Dimers, Komatsu K, The 5th International Symposium on Green Chemistry in China, 23 May, Hefei, China.

Radical Cation and Dication of Sulfur-Containing π-Electron Systems Stabilized by Rigid σ-Frameworks, Nishinaga T, Komatsu K, et al., The 5th International Symposium on Functional π-Electron Systems, 1 June, Ulm, Germany.

Fullerene-Based Nanomaterials, Komatsu K, The 12th International Symposium on Supramolecular Chemistry, 7 October, Eilat, Israel.

Structure and Properties of a Novel Fullerene Dimer $RC_{60}$-$C_{60}R$ and Facile Generation of Fullerenyl Cation $RC_{60}^{+}$, Cheng F, Murata Y, Kitagawa T, Komatsu K, Gordon Research Conference, 29 July, Aioi, Japan.

### Grants

Komatsu K, Appearance of biradical character in π-conjugated hydrocarbons by annelation with strained bicyclic frameworks, Grant-in-Aid for Scientific Research (B) (2), Apr. 2002 - Mar. 2004.

Kitagawa T, Construction of fullerene-coated nanostructures using alkylfullerenyl cations, Grant-in-Aid for Scientific Research (C) (2), Apr. 2002 - Mar. 2004.

Nishinaga T, Design and synthesis of π-conjugated oligomers folded in helical structure by electron transfer, Grant-in-Aid for Encouragement of Young Scientists (A), Apr. 2002 - Mar. 2004.

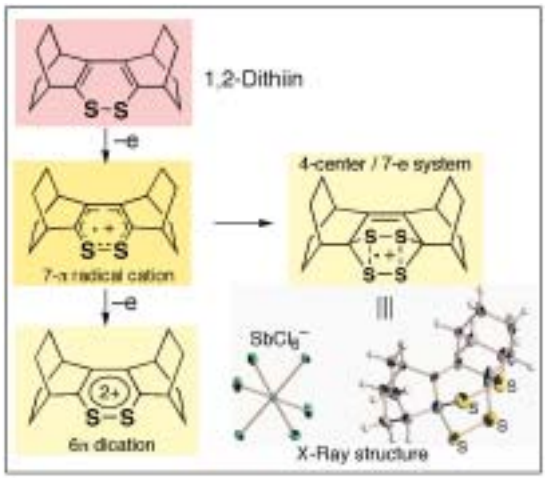
Murata Y, Synthesis of endohedral fullerenes by the use of organic chemistry, Grant-in-Aid for Encouragement of Young Scientists (A), Apr. 2002 - Mar. 2004.

Kitagawa T, Construction of nano-electronic devices based on precise molecular design, CREST, Japan Science and Technology Corporation, Nov. 2002 - Oct. 2007.

Murata Y, Komatsu K, Application of functionalized fullerenes for fabrication of solar cells, Academic-Industrial Cooperative Research Fund, Aug. 2002 - Jul. 2003.

## Formation of the First Stable Radical Cation Having a Tetrathia 4-Center/7-Electron Bond

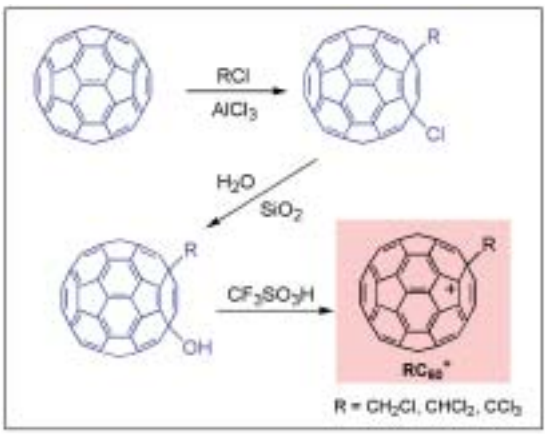
Annelation of cyclic π-conjugated systems with rigid bicycloalkene framewoks has been shown to stabilize the π-system when it is positively charged, both by the σ-π conjugation and steric protection effects. Thus, the radical cation and dication of 1,2-dithiin (1,2-dithia-3,5-cyclohexadiene) were generated as stable species by this structure modification for the first time. Furthermore, the radical cation was found to disproportionate to give a totally new radical cation having the tetrathiabicyclic structure, which is remarkably stabilized by a strong transannular interaction among four sulfur atoms forming a novel 4-center/7-electron system, together with a thiophene derivative.[1]




1. Wakamiya A, Nishinaga T, Komatsu K, *J. Am. Chem. Soc.*, **2002**, *124*, 15038.

## Generation and Thermodynamic Stabilities of Alkylfullerenyl Cations

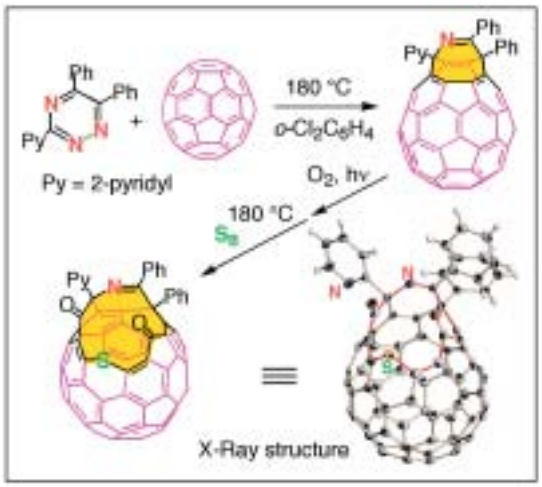
The generation and the direct observation of functionalized fullerenyl cations have been considered a challenging task, owing to the electronegative nature of the $C_{60}$ cage. We could generate monoalkylated fullerenyl cations ($RC_{60}^+$, R = chloroalkyl group) as long-lived ions by treating the corresponding fullerenol precursors with a strong acid. Spectral analysis showed that these cations have structures with $C_s$ symmetry and their positive charge is mainly located on C-2. Kinetic studies of the $S_N1$ solvolysis of the corresponding chlorides and the equilibrium constants of the hydrolysis to form fullerenols indicated that the cations $RC_{60}^+$ have stabilities comparable to that of the *tert*-butyl cation.[2]




2. Kitagawa T, Lee Y, Komatsu K, et al., *Chem. Commun.*, **2002**, 3062.

## Synthesis of a Novel Open-Cage Fullerene Derivative with a 13-Membered-Ring Orifice

As the first step in a novel approach to endohedral fullerene complexes, which are expected as nano-scale materials with unique properties, organic synthesis of open-cage fullerenes is quite important. When a thermal reaction of $C_{60}$ with a 1,2,4-triazine derivative was conducted, a [4+2] cycloaddition followed by nitrogen extrusion took place to give a derivative with an 8-membered-ring orifice. This orifice was further enlarged by photochemical oxidation followed by sulfur insertion to the rim of the orifice to give a totally new open-cage fullerene derivative with a 13-membered-ring opening, which is the largest orifice reported so far. A preliminary experiment indicated that it is quite promising to incorporate small molecules into the inside of this fullerene cage.[3]




3. Murata Y, Murata M, Komatsu K, *Chem. Eur. J.*, **2003**, *9*, in press.